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AFATL-TR-73-13

NEW PYROTECHNIC BINDERS

**ROCKETDYNE DIVISION
NORTH AMERICAN ROCKWELL CORPORATION**

TECHNICAL REPORT AFATL-TR-73-13

JANUARY 1973

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New Pyrotechnic Binders

C. L. Hamermesh


E. F. Witucki

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FOREWORD

This study was conducted by Rocketdyne, a Division of Rockwell International Corporation, 6633 Canoga Avenue, Canoga Park, California 91304, under Contract F08635-72-C-0143 with the Air Force Armament Test Laboratory, Eglin Air Force Base, Florida 32542. Mrs. Sandra M. Lefstad (DLIP) was Project Monitor for the laboratory. This report covers work performed during the period from April 1972 to January 1973. Principal investigator for Rocketdyne was Dr. C. L. Hamermesh with support from Mr. E. F. Witucki. This report has been designated Rocketdyne Report No. R-9161.

This technical report has been reviewed and is approved.


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ABSTRACT

Low-cost liquid polymers of high oxygen content (>45 percent) have been prepared. Curing behavior of combinations of the polymers and cross-linking agents has been evaluated as well as the mechanical properties of the cured materials. Compatibility with pyrotechnic ingredients was determined as well as castability of pyrotechnic compositions containing such polymers. The high level of behavior exhibited by the polymer systems indicates that they possess considerable potential for use in the development of castable pyrotechnic formulations that will exhibit a high level of performance in regard to color quality and illumination.

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SECTION I

INTRODUCTION

Pyrotechnic compositions contain a very high proportion of solid ingredients. To maintain structural integrity, small quantities of a liquid matrix material (binder) are included, but at low binder levels, the pyrotechnic is still quite dry. Therefore, to obtain a coherent product, processing must consist of a series of pressings to produce the end item. This kind of manufacturing technique presents problems in sensitivity hazards during pressing as well as from the dusting that can occur when dry materials are processed.

Increasing the liquid binder content reduces both difficulties and improves processability. Thus, for example, in the LUU-2 flare, a higher quantity of a liquid polymer provides sufficient fluidity so that a tamp-cast product is obtained. However, this binder system has several shortcomings that limit its use in attaining a castable pyrotechnic. These include the relatively low oxygen content of the polymer (ca. 40 percent), the high viscosity (35 to 50,000 cps), and the presence of undesirable carboxyl groups on the polymer.

To obtain a castable system, larger quantities of a liquid binder must be employed. However, if the binder system is high in carbon content and relatively low in oxygen, upon combustion the carbon, which has not been oxidized, becomes incandescent and degrades both the color quality in a colored flare and the light output from an illuminating flare. Therefore, it is imperative that the polymer have an oxygen content high enough to combust all the carbon. In addition, the polymer must be compatible with considerations of cost and mechanical properties. This rules out the use of high oxygen content plasticizers that are costly and also may exude from the pyrotechnic and change the mechanical properties. It would be preferred that a polymer with an oxygen content in excess of 45 percent and preferably 50 percent or higher be employed.

Castability is a function of polymer fluidity (i.e., viscosity). Therefore, a low-viscosity material is desirable. The high viscosity of the LUU-2 binder may be the limiting factor in obtaining a castable pyrotechnic. This situation is probably worsened by the carboxyl groups on the polymer chain that interact physically with the solids and further reduce the fluidity.

This report documents a study to develop low-cost, low-viscosity binders of high oxygen content that can serve as the means for obtaining castable pyrotechnics. This effort included the synthesis of low-cost liquid polymers of high oxygen content, evaluation of the curing behavior, mechanical properties, and compatibility with pyrotechnic ingredients of such binders, and, finally, a preliminary evaluation of the castability of formulations containing these binders.

SECTION II

SUMMARY

Selection of the polymer systems was based on the following criteria:

1. The polymers should have an oxygen content in excess of 35 percent and be of low viscosity and curable.
2. The curing of the polymer-curative combination should be compatible with conventional pyrotechnic manufacturing procedures.
3. The binder should be compatible with pyrotechnic ingredients.

On this basis, three polymer systems were selected for study:

1. The polyester from the reaction of diethylene glycol with diglycolic acid (48 percent oxygen)
2. Poly (alkylene carbonates) of high oxygen content prepared by the reaction of phosgene with glycol. If diethylene glycol (DEG) is used, the oxygen content is 48 percent. If ethylene glycol (EG) is used, the oxygen content is 54 percent.
3. Copolymers of acrylate esters with vinyl acetate that are subsequently hydrolyzed at the acetate group and then esterified with nitric acid (46 to 51 percent oxygen depending on the molar ratio in the copolymer).

Liquid products were obtained from both the polyester and polycarbonate systems. It should be noted that this is the first report of the preparation of liquid polycarbonates. The copolymer approach yielded only taffy-like solids and was abandoned.

Curing behavior of hydroxyl-terminated liquid polyesters and polycarbonates was evaluated using a polyisocyanate, PAPI, as the cross-linking agent. Satisfactory cures could be obtained even at ambient temperatures after 72 hours. The exotherm observed under such conditions was 1°F. These results, as well as the adequate pot life exhibited, indicate that the binders are compatible with conventional pyrotechnic manufacturing procedures.

Mechanical properties of the cured binders are excellent with elongations of more than 500 percent and compression strengths in excess of 7500 psi. Shrinkage was less than 1 percent. The compatibility of these polymers with various pyrotechnic ingredients as well as in pyrotechnic formulations was evaluated. In vacuum stability tests at 70°C, less than 1.1 cc of gas was generated per gram of composition in 48 hours. This represents a high level of compatibility.

As a final phase of this program, the effect of viscosity of the polymers on the castability of a pyrotechnic formulation containing the polymers was determined. At 140°F, all formulations were castable regardless of the polymer viscosity (5000 to 59,000 cps). However, those containing the lower viscosity binders exhibited solids separation.

The results obtained under this program represent a significant first step toward the development of practical, low-cost, castable pyrotechnic compositions.

SECTION III

DISCUSSION

In examining potential polymer systems for use in this program, the contractor was governed by the criteria that had been explicitly established in the Request for Proposal (RFP) that led to this study. The following criteria were included:

1. The system shall have an oxygen content in excess of 35 percent, be of low viscosity at room temperature, be curable, and be of low toxicity.
2. Pot life shall be at least 6 hours at ambient.
3. Curing temperatures may not exceed 80°C nor require more than 72 hours, and any exotherm may not exceed 250°C.
4. On curing, shrinkage shall be less than 1 percent, and the product obtained shall possess good mechanical properties over a wide temperature range.
5. The binder shall be compatible with a wide variety of ingredients commonly employed in pyrotechnic compositions.

An additional consideration alluded to in the RFP was cost.

Based on the oxygen content requirement, the desirable oxygen containing structures that should be present in the polymer chain would include ether

linkages (-O-), esters ($\text{-}\overset{\text{O}}{\parallel}\text{CO-}$), carbonates ($\text{-O-}\overset{\text{O}}{\parallel}\text{C-O-}$), nitro groups (-NO_2), and nitrate species (-ONO_2). For polymers of equal oxygen content, the latter two moieties would be preferred because there is less carbon to oxidize. However, this advantage is considerably diminished in that such groups make the polymer more sensitive to friction and impact as well as more costly to prepare. Therefore, if these groups are to be incorporated into the polymer, their number must be limited and the synthesis route must be simple, straightforward, and inexpensive.

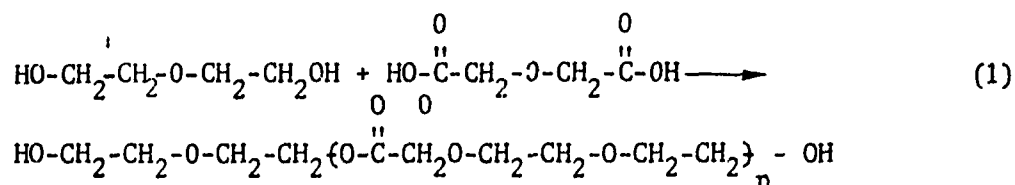
In regard to the nature of the carbon skeleton between the oxygen moieties, it was concluded that aliphatic groups were preferred. Aromatic groups introduce rigidity into the polymer and reduce the likelihood of obtaining a liquid product. There is also some evidence that the reduced color quality observed when pyrotechnic formulations containing aromatic compounds or polymers are burned is the result of the incomplete combustion of the aromatics, probably due to lack of oxygen.

A final consideration for polymer selection is the nature of the functional groups on the polymer that are to be used in cross linking the polymer after pyrotechnic manufacture. As in solid propellants, a curing reaction is required in which no byproducts are generated. The use of carboxyl groups for curing purposes was rejected both because of considerations discussed previously as well as the reported interaction of such species with magnesium.

For this reason, polymers containing pendant or terminal hydroxyl groups were selected with the curative of choice an isocyanate-containing compound.

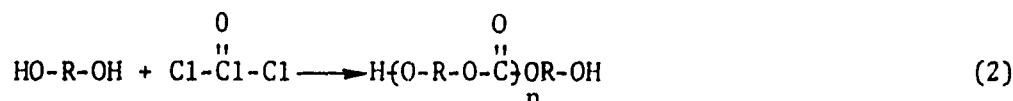
Using these criteria, three polymer systems were selected for study under this program:

1. The polyester from the reaction of diethylene glycol (DEG) and diglycolic acid [Equation (1)]:



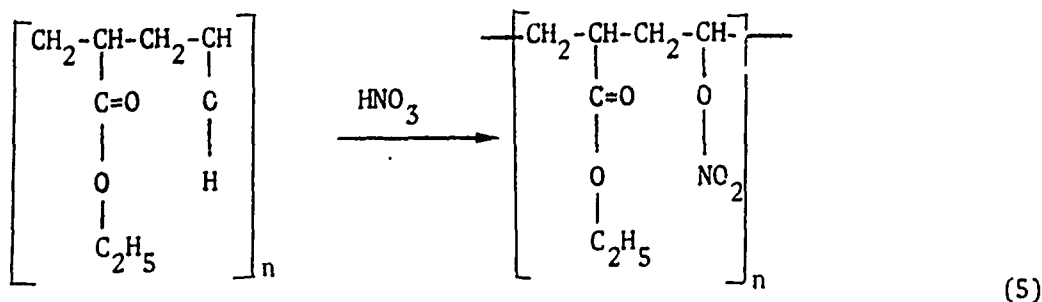
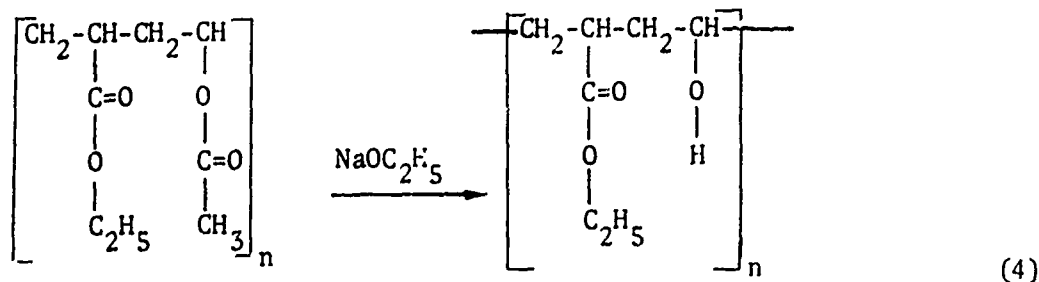
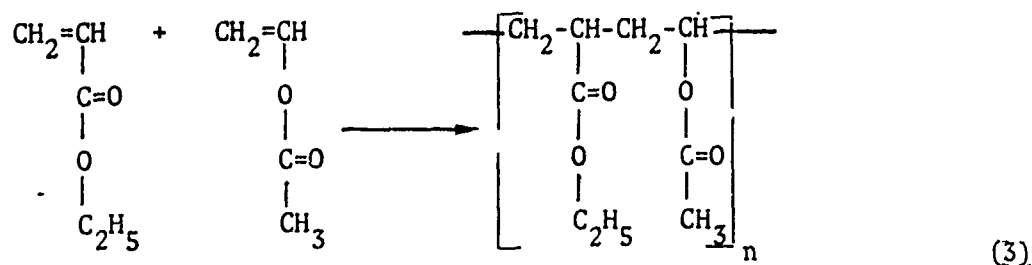
This polymer contains approximately 48 percent oxygen.

2. A poly (alkyl carbonate) prepared by the reaction of a glycol with phosgene [Equation (2)]:



When DEG is the glycol, the oxygen content of the polymer is 48 percent. If ethylene glycol (EG) were employed, the oxygen content rises to 54.5 percent.

3. The product from the copolymerization of an acrylate and vinyl acetate [Equation (3)] which is hydrolyzed [Equation (4)] and then reacted with nitric acid [Equation (5)]:



Depending on the molar ratio of acrylate ester to vinyl acetate employed, the oxygen content of this polymer would range from 46 to 51 percent.

POLYMER SYNTHESIS

Polyesters

The reaction of diglycolic acid and various glycols is well known. Polymer preparation is relatively simple and involves a reaction at elevated temperatures (125-180°C) until the acid number of the polymer reaches a predetermined value. (Acid number is a measure of the extent of reaction and of the polymer molecular weight. It is obtained by titrating the reaction mixture with base.) For details of preparation of polymers, see the Experimental section.

As indicated previously, the glycol employed was DEG. The major parameter examined for the polymer when $n = 5$ in Equation (1) was the effect of the extent of reaction (as measured by the acid number) on the viscosity of the product. For polymers of varying acid number obtained from a reaction mixture in which the ratio of glycol to diacid was 6:5, the following results were obtained:

<u>Acid Number of Polymer</u>	<u>Viscosity, cps</u> ^(a)	<u>Molecular Weight</u> ^(b)
18	32,000	874
31	22,800	765
48	5,300	659

(a) Brookfield viscosity, average of two readings at different speeds

(b) By ebulliometry

These results are as expected in that the molecular weight varies inversely as the acid number. Since molecular weight and viscosity are directly related, the product with the lowest acid number should have the highest molecular weight and viscosity.

The calculated molecular weight for the product from the 6:5 glycol-diacid reaction [in Equation (1), $n = 5$] is 1126. However, this calculation assumes that all ingredients were pure. The diglycolic acid used was of the practical grade in order that polymer cost could be kept at a level that is realistic in regard to the end use application. It would not be unusual to have both monofunctional and nonfunctional material present in the diglycolic acid. The former species will alter the stoichiometry of the esterification reaction in addition to acting as a chain-terminating agent. In either event, this will yield a product of lowered molecular weight. If not removed from the polyester, nonfunctional compounds will also lower the molecular weight. Since there is no work-up of the polyester after preparation to remove such impurities, it would not be surprising if some of the nonfunctional material were present in the samples submitted for analysis.

Elemental analysis of one of these polyesters gave a carbon content of 45.78 percent, hydrogen 6.33 percent, and oxygen (by difference) of 47.89 percent. Calculated oxygen content for the polymer is 46.88 percent. Infrared spectra of all three products (Figure 1) were identical and exhibited the features anticipated, i.e., carbonyl and hydroxyl peaks.

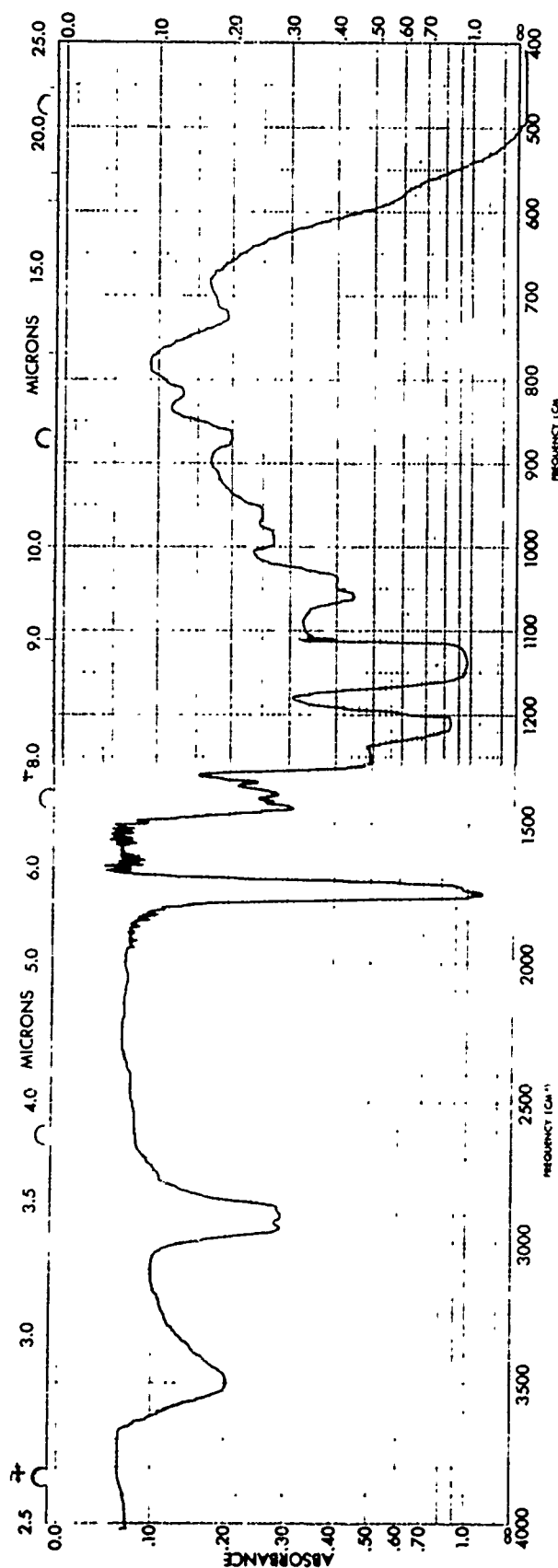
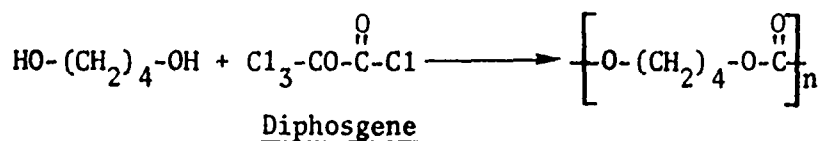


Figure 1. Infrared Spectrum of Polyester

Scaleup of this polyester to a batch as large as five pounds was accomplished with no difficulty, and the product was identical in all respects to that obtained from smaller batches.

Polycarbonates

The high oxygen content available in this system made these polymers very attractive. However, no report exists on the preparation of liquid products. In fact, the only literature reference to synthesis of wholly aliphatic polycarbonates is a German patent by H. Willersinn [Reference (1)] in which butylene glycol is employed with diphosgene.



The product was reported to have a softening point of 50 to 60°C. It, therefore, appeared that, with the proper choice of glycol (such as DEG), liquid products might result. Furthermore, in reading the patent in its entirety, it became obvious that diphosgene had been used rather than phosgene, primarily to obtain high molecular weight products. However, for pyrotechnic applications, low molecular weight liquid products are desired. Therefore, it appeared that phosgene might serve as a better intermediate than diphosgene. An additional advantage of this approach is the low cost and commercial availability of the former.

Initial experiments to prepare the polycarbonate [in Equation (2), $n = 5$] were run in which phosgene was bubbled into a solution of glycol in benzene and pyridine. (The latter is used as a basic scavenger for HCl generated in the reaction.) From this reaction, a liquid product was obtained in low yield. The infrared spectrum gave the characteristic peaks for a carbonate. Thus, a new class of liquid polymers of high oxygen content, the polycarbonates, has now been reported.

Yield of the polycarbonate is significantly affected by the temperature at which the reaction is maintained after phosgene addition is complete. At 10°C, yields were low (10 to 15 percent). At 70 to 80°C, yield rose to 55 to 75 percent. (See Section V for preparative details).

Replacement of benzene with chloroform gave approximately the same yield of polymer, the infrared spectrum (Figure 2) of which was identical to that for the polymer using benzene as a solvent.

The only factor affecting product yield and purity is the workup procedure. At the end of the reaction, large amounts of pyridinium hydrochloride are present. Removal at this point is desirable in that this salt interfered with subsequent workup and led to reduced yields. Because of the hygroscopic nature of the salt, it was found desirable to filter the reaction mixture under a blanket of nitrogen to avoid water uptake by the salt. If water is present, the salt becomes sticky and in this form it interferes with the workup and reduces the yield by retaining absorbed polymer. As a final step to remove traces of pyridine from the product, the polymer was stripped at 50°C under full vacuum for several hours. (A modification of this procedure as a result of mechanical properties testing is presented below.)

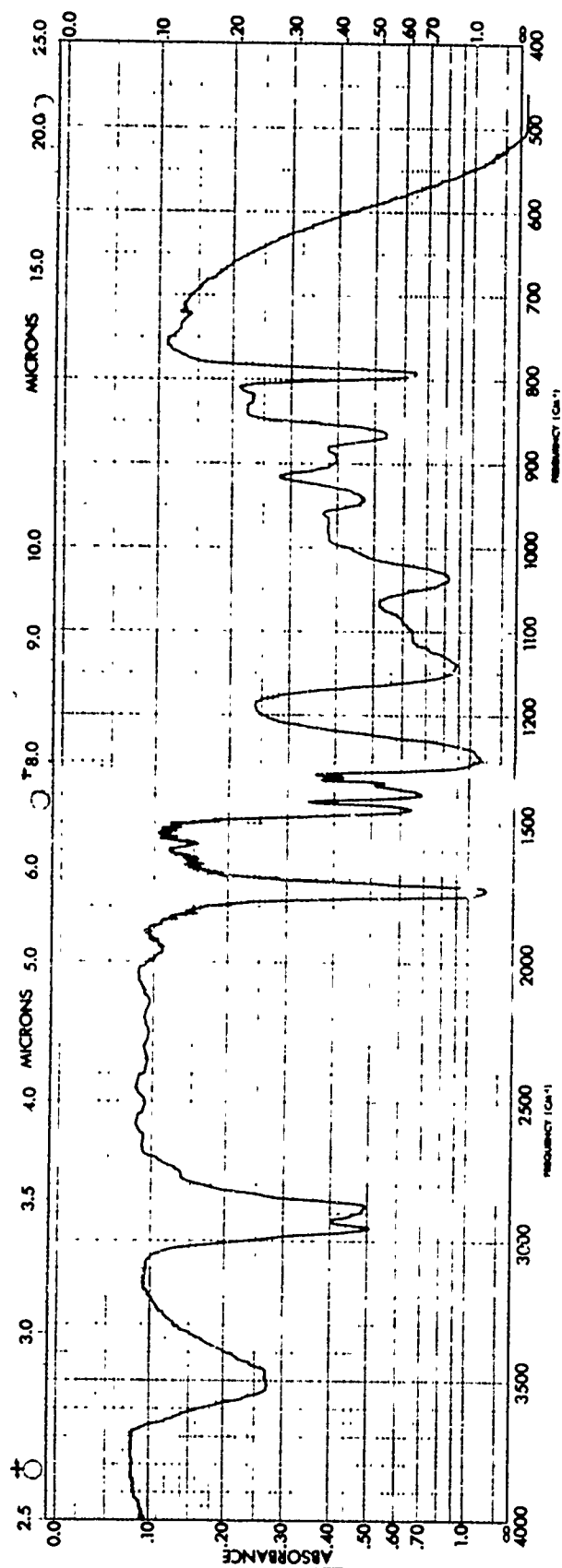
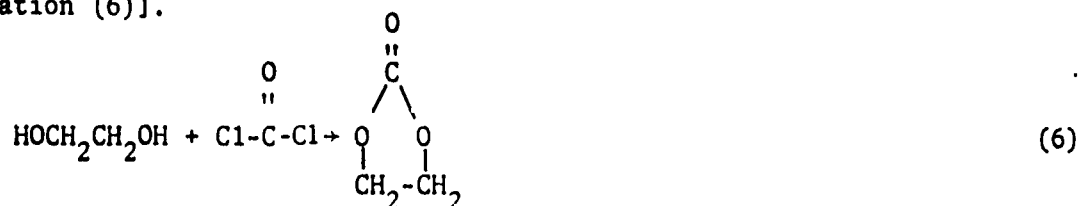


Figure 2. Infrared Spectrum of Polycarbonate

Analyses of polycarbonates from duplicate runs were good, and the infrared spectra gave the anticipated characteristic ester and hydroxyl peaks. Molecular weight as determined by ebulliometry was in excellent agreement with the calculated value (729 obtained, 760 theoretical). Scaleup of the polymer to the 1 to 2-pound level gave products of comparable viscosity and infrared spectra to those obtained in smaller runs.

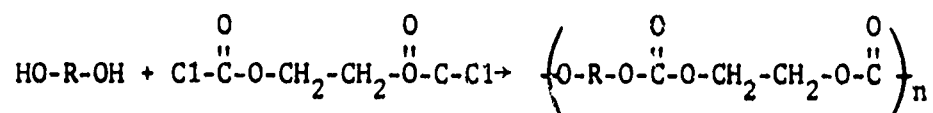
The effect of reaction stoichiometry on the polymer viscosity was examined to a limited extent. As expected, the product from the 11 glycol-to-10 phosgene reaction had a higher viscosity while the polymer from the 4 glycol-to-3 phosgene reaction had a slightly lower value.

Another route that was pursued somewhat more extensively than the effect of stoichiometry was that of increasing the oxygen content of the polymers by replacing DEG, either entirely or partially, with ethylene glycol. Products with very low viscosities resulted. For example, 50-percent replacement of DEG with EG gave a very fluid polymer (1235 cps). Total replacement produced a 20-cps liquid that solidified on standing to a low-melting solid. While elemental analysis was in agreement with calculated values and infrared spectra comparable to those obtained previously for DEG polycarbonates, molecular weights were very low. For example, the 50 ethylene glycol-to-50 DEG polymer measured 330, theoretical 575; the total replacement of DEG measured 120, theoretical 540. These results were confirmed in duplicate experiments and led to the conclusion that in the reaction of phosgene with ethylene glycol, cyclic products are produced, i.e., ethylene carbonate [Equation (6)].



The properties of ethylene carbonate are analogous to those of the low-melting solid obtained from the ethylene glycol reaction.

In the hope of avoiding the cyclization reaction, phosgene was replaced with ethylene bischloroformate [Equation (7)].



Runs were made with both DEG and EG and at stoichiometries where molecular weights of 500-to-700 should result. Measured molecular weights of the product were indeed in the anticipated range; however, viscosities of the liquid products were extremely high (480,000 cps for the DEG polycarbonate and 935,000 cps for the EG polycarbonate). Such high viscosities are difficult to reconcile with the low polymer molecular weight. It may be that even under the reaction conditions employed cyclization is occurring, and cyclic polycarbonates have a much higher viscosity than open chain polymers of similar molecular weight. Further study of these potentially valuable polymers is required to clarify this point as well as provide a route for obtaining these polymers as low viscosity liquids of reasonable molecular weight.

Polyacrylates

The product from the approach outlined in Equations (3), (4), and (5) contains the nitrate ester group that is reported to enhance the performance of pyrotechnics. The possibility of obtaining a high oxygen content polymer with such groups by a synthetic route that is relatively low cost made this approach attractive. However, it involves three reactions to obtain the desired product. Therefore, it is essential that the product from the first reaction, the copolymerization of the acrylate ester and vinyl acetate, must be very fluid since the structural changes affected in steps 2 and 3 will lower the fluidity. Initial experiments involved the copolymerization in benzene of equimolar quantities of ethyl acrylate and vinyl acetate. Conversion of monomer to polymer was no higher than 70 to 75 percent, and the products obtained were taffy-like solids. No significant improvement in fluidity was obtained when chain transfer agents were used to reduce polymer molecular weight. Chain transfer agents such as dodecyl mercaptan operate to lower the polymer molecular weight by reacting with the growing chain to terminate it prematurely and thus reduce the molecular weight.

A quantitative yield of polymer was obtained when a change in polymerization technique was made. This involved polymerization in emulsion with water as the external phase. Unfortunately, the emulsion technique produces a polymer of higher molecular weight than that obtained from solution. Therefore, polymer fluidity was not improved by this change. Again, the use of increased quantity of chain transfer agent did not result in a liquid product.

In analyzing some of the factors that affect the fluidity of a polymer, it is obvious that the glass transition temperature of the polymer is important. With a low T_g , a good probability of obtaining a liquid product exists, assuming that the molecular weight is of relatively low value (ca 1-2,000). For a copolymer, the glass transition temperature T_{g_c} can be calculated from

$$\frac{1}{T_{g_c}} = \frac{m_1}{T_{g_1}} + \frac{m_2}{T_{g_2}}$$

where

T_{g_c} = glass transition temperature of the copolymer

T_{g_1} = glass transition temperature of the homopolymer of monomer 1

T_{g_2} = glass transition temperature of the homopolymer of monomer 2

m_1 = mole fraction of monomer 1

m_2 = mole fraction of monomer 2

Using this equation, the effect of various acrylate esters of different T_g on the T_{g_c} of the copolymer with vinyl acetate was calculated and is given in Table I.

TABLE I. EFFECT OF MONOMER RATIO ON COPOLYMER GLASS TRANSITION TEMPERATURE

Monomer Mole Fraction				T_{g_c} , °C Calculated
Ethyl Acrylate ($T_g = -23^\circ\text{C}$)	Methyl Acrylate ($T_g = 0^\circ\text{C}$)	Butyl Acrylate ($T_g = 70^\circ\text{C}$)	Vinyl Acetate ($T_{g_c} = 100^\circ\text{C}$)	
0.5	--	--	0.5	21
0.25	--	0.25	0.5	11
--	0.25	0.25	0.5	17
--	0.125	0.375	0.5	2
--	--	0.4	0.6	11
--	--	0.5	0.5	-10

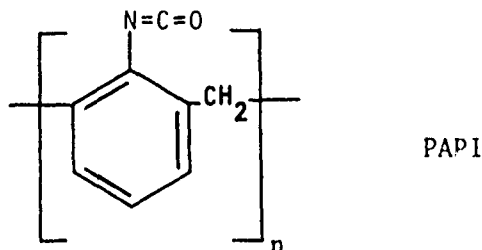
It is seen that total replacement of ethyl acrylate with the butyl ester should result in a liquid polymer. However, the higher carbon content that accompanies the exclusive use of the butyl ester will lower the oxygen content of the final polymer. To overcome this, a portion of the butyl ester should be replaced with methyl acrylate. The terpolymer (0.375 butyl acrylate to 0.125 methyl acrylate to 0.5 vinyl acetate) was prepared. It was liquid and had a viscosity of 100,000 cps. As in previous experiments with solution polymers, additional transfer agent did not lower polymer viscosity significantly.

Based on a patent of Rohm and Haas [Reference (2)] in which the acetate group of an acrylate-vinyl acetate copolymer is preferentially hydrolyzed, the liquid terpolymer was reacted under these conditions [Equation (4)]. The taffy-like product obtained exhibited a large hydroxyl peak in the infrared spectrum. Esterification with fuming nitric acid, as per Noma [Reference (3)], gave a material whose infrared spectrum had no hydroxyl peak but showed rather a large nitrate ester peak was present. However, the polymer was still a taffy-like solid. At this point, it was concluded that this approach was unlikely to yield a liquid product. Therefore, with the concurrence of the cognizant program project engineer, attempts to obtain liquid polymers containing nitrate esters by means of this synthesis route were abandoned.

Polymer Synthesis Summary

It is apparent from the work done on the two successful polymer systems, the polyester and polycarbonate, that additional work remained to be done in regard to the polymer synthesis. (See Section IV of this report.) However, since the objective of the program was to establish as rapidly as possible the potential utility of the polymers for pyrotechnic applications, polymers representative of the two successful systems were selected for further evaluation, although it was recognized that they might be far from optimum in some respects.

Curing Behavior. The first step in this study was to determine if the polymer could be cured under conditions compatible with pyrotechnic manufacturing processes. As indicated previously, the selection of hydroxyl groups as the reactive functional groups on the polymer chain required that an isocyanate-containing species be employed as the crosslinker. As a matter of convenience, a polyisocyanate, polyaryl polyisocyanate, PAPI was employed.



PAPI

It was recognized that this curative is not ideal because of the aromatic structures present; however, its ready availability made its use convenient.

Three polymers were employed in the initial study. Two were polyesters (6:5 glycol-diacid); [Equation (1), $n = 5$], one of high acid value (47), the other of lower acid value (17). The third polymer was a polycarbonate from the 6:5 reaction of DEG-phosgene [Equation 2, $n = 5$]. Curing behavior was evaluated at three NCO/OH levels and at three curing schedules: 175°F for 1 hour, 130°F overnight, and ambient temperature for 72 hours (Table II).

At 175°F, the polycarbonate and the low acid number polyester samples cured. Samples of the other polyester, besides not curing, showed signs of bubbling. Therefore, this polyester was dropped from further testing. When kept at 130°F overnight, all samples of both the polycarbonate and the polyester combinations cured with the exception of the 0.85 NCO/OH mixture for the polyester. At ambient, curing occurred for the two higher NCO/OH ratio polycarbonate-PAPI mixtures, but only for the 1-to-1.5 ratio polyester system. Several days later all the polycarbonate samples had cured, but no change had occurred in the polyester system.

Curing of both polymers at times and temperatures compatible with conventional pyrotechnic manufacturing conditions led to an examination of both the pot life of the polymer cross-linker combination and the peak exotherm exhibited by these conditions during curing.

Pot life of the polymer-curative combination was determined by mixing these materials at ambient temperature and measuring the viscosity of the mixture as a function of time.

TABLE II. CURING BEHAVIOR OF POLYESTERS AND POLYCARBONATES

Polymer	NCO/OH	Cure Schedule		
		175°F - 1 Hour	130°F - Overnight	Ambient - 72 Hours
Polyester (high acid) number	0.85	Bubbling, no cure	---	---
	1.0	Bubbling, no cure	---	---
	1.15	Bubbling, no cure	---	---
Polyester (low acid number)	0.85	Cured	No cure	No cure
	1.0	Cured	Cured	Cured
	1.15	Cured	Cured	Cured
Polycarbonate	0.85	Cured	Cured	No cure
	1.0	Cured	Cured	Cured
	1.15	Cured	Cured	Cured

*Not Tested

<u>Polymer</u>	<u>Viscosity (cps) After</u>					
	<u>0 Hour</u>	<u>1 Hour</u>	<u>2 Hours</u>	<u>4 Hours</u>	<u>5 Hours</u>	<u>6 Hours</u>
Polyester	25,400	950,000	1,800,000	2,900,000	4,000,000	4,400,000
Polycarbonate	8,200	330,000	1,600,000	3,920,000	6,720,000	7,440,000

As expected, a considerable rise in viscosity occurred during the 6-hour period. However, extrapolation of these data for the polymer-curative mixture as a means for predicting the pot life and castability of pyrotechnic formulations containing these polymers is replete with such uncertainty as to make these predictions guesses at best. From the contractor's experience with solid propellant formulations where viscosities of such compositions are very high, it would appear that pot life of the pyrotechnic should be adequate.

The temperature rise during curing was determined by means of thermocouple embedded in the polymer-curative combination. Starting at 79°F (the mix temperature), the temperature rose only 1 degree at maximum during the succeeding 24-hour period.

EVALUATION

Mechanical Properties

Dogbone samples were prepared from mixes of the polymers and curative. Early samples exhibited evidence of bubbling and voids. These voids were much more apparent in the polyester than the polycarbonate. It was concluded that this was the result of water being present in the polymer and reacting with the isocyanate to produce carbon dioxide. This was confirmed indirectly when dogbones fabricated from polymers stripped for 4 hours under vacuum at 70 to 80°C did not show evidence of bubbling.

For these tests, the polymers were mixed with curative at the 1-to-1 NCO/OH level and cast into dogbone molds (gage length - 1.70 inches, cross section - 1/4 by 1/4).

For compression tests, samples were cast into 1-inch cube molds. Other samples were placed in shrinkage molds (1/2 by 1/2 by 5 inches). Tensile, elongation, and compression properties were measured at ambient on an Instron testing machine and are given in Table III.

TABLE III. MECHANICAL PROPERTIES OF POLYMER-CURATIVE COMBINATION

<u>Polymer</u>	<u>Tensile Strength, psi</u>	<u>Elongation, %</u>	<u>Compressive Strength, psi</u>	<u>Shrinkage, % Change</u>
Polyester	50 ^a	1100 ^a	>7500	1 ^b
Polycarbonate	62	480	>7500	1 ^b

^aSlightly undercured sample.

^bEstimated value due to rubbery nature of product.

These properties are excellent, and it would be reasonable to expect a transition of such behavior for pyrotechnics containing such binders.

Compatibility Studies

Even more important than curing behavior and mechanical properties, a pyrotechnic composition must be composed of completely compatible materials. Therefore, the compatibility of the two polymers was evaluated with a variety of pyrotechnic ingredients. Included in the tests were potassium chlorate, potassium perchlorate, strontium chloride, sodium nitrate, barium nitrate, and magnesium (four grades).

The compatibility study was carried out in three stages: spot plate tests, hot stage microscope tests, and vacuum stability tests. In the first stage, the individual ingredients were mixed with the polymer at ambient temperature on a spot plate. The mixtures were examined over a 1-hour period for evidence of bubbling or discoloration. No reaction was observed with either polymer and any ingredient. When the curative PAPI was tested in a similar manner, there again was no evidence of reaction. In the second stage, the polymer (or curative) was mixed with the ingredient, transferred to a microscope slide, and placed in the hot stage of a Rickert microscope. The cavity was closed, and the temperature was raised to 250°F. The sample was observed visually throughout the heating cycle for any evidence of bubbling. There was no reaction in any combination.

For the vacuum stability test, a Talianni apparatus was employed. The polymer and curative were mixed with the pyrotechnic ingredients and then transferred to an ampoule of known volume. The ampoule was attached to a mercury gas buret and heated in a 70°C oil bath for 48 hours. Gas evolution was monitored throughout this period. The results of these tests are given in Table IV.

TABLE IV. VACUUM STABILITY TESTS (70°C)

<u>Ingredient Employed</u>	<u>cc gas generated/g/48 hours</u> <u>Polymer System</u>	
	<u>Polyester</u>	<u>Polycarbonate</u>
Polymer + curative	0.98	0.84
Polymer + curative + $KClO_3$ (30:70)	0.48	0.44
Polymer + curative + Mg (30:70)	0.41	0.44
Yellow flame formulation ^a	0.36	0.49
Red flame formulation ^b	1.1	0.49
Green flame formulation ^c	0.47	0.80

^aYellow flame formulation - 15% Mg, 65% $NaNO_3$; 20% binder (see d)

^bRed flame formulation - 46% $Sr(NO_3)_2$, 18% NH_4ClO_4 , 12% $SrCl_2$, 20% binder (see d)

^cGreen flame formulation - 11.76% $BaCO_3$, 60% $Ba(ClO_3)_2$, 28.24% (see d)

^dBinder weight is total for polymer and curative.

The low level of gas evolution is extremely encouraging. For example, in solid propellants, a composition that generates less than 2 cc of gas per gram of composition in 48 hours is considered an acceptable, compatible composition.

Evaluation Summary

Having determined that the curing behavior, mechanical properties, and compatibility of these polymers were satisfactory, the contractor prepared and submitted to the AFATL, as a partial fulfillment of the contractual requirements, a Characterization Report (Appendix I) summarizing these results. In discussion with cognizant Air Force personnel, it was mutually agreed that these properties of the binders were eminently suitable for pyrotechnic applications with the possible exception of the viscosity. It was felt that these values might be too high to yield castable pyrotechnic formulations. However, since studies of the castability of solid propellant compositions had shown that binder systems of even higher viscosities yielded castable products, it was agreed that a preliminary study of the castability of pyrotechnics made with these binders should be performed.

CASTABILITY STUDIES

At the request of the Air Force, the first phase of this effort involved investigation of means for reducing the viscosity of the polymer.

Three approaches were employed in attempting to produce lower viscosity materials: (1) dilution with reactive solvents, (2) changes in monomer stoichiometry, and (3) changes in starting materials. In the first approach, glycols, such as diethylene glycol, triethylene glycol, glycerin, and ethylene glycol, were added to both the polyester and polycarbonate. The levels of glycol employed were 5, 10, and 15 parts per 100 of polymer. Glycols were employed because the hydroxyl groups would react in the curing process and thus be incorporated into the crosslinked matrix. In all cases, the diluents reduced the polymer viscosity with ethylene glycol being the most effective. One shortcoming of this approach is that the hydroxyl equivalent for the combined system is decreased and markedly so at diluent levels greater than 5 parts per 100. This results in a larger quantity of crosslinker used in the curing, which will lower the overall oxygen content of the polymer-crosslinker combination. It is the contractor's opinion that the diluent approach is an inferior means for reducing polymer viscosity.

As indicated previously, viscosity is a function of polymer molecular weight. For the 6-to-5 DEG-diglycolic acid polyester (acid number = 20), the viscosity was 32,000 cps. Changing the stoichiometry to 4-to-3 (acid number = 9) reduced the viscosity to 13,800 cps. Based on the contractor's experience, it is estimated that the latter polymer (acid number = 20) would have a viscosity below 10,000 cps.

The most significant change occurred when DEG was totally replaced with triethylene glycol (TEG) in these compositions. In the 6-to-5 polyester, for products of comparable acid values, this change resulted in a viscosity drop from 32,000 to 10,000 cps. For the 4-to-3 polyester containing TEG, products with viscosities of 5000 to 8250 cps were obtained depending on the acid value of the product. Similar effects were observed in the polycarbonate system. For the 4-to-3 glycol to phosgene product, use of TEG brought the viscosity to 12,000 cps.

Use of the TEG instead of DEG is not an unmixed blessing in that the oxygen content of the polymer is reduced by 2 percent. Therefore, in the castability study, polymers of both types were evaluated. They included

1. 6-to-5 DEG-DGA polyester; acid Number = 17; 31,000 cps (25°C)
2. 6-to-5 polycarbonate of TEG and phosgene-26,000 cps (24°C)
3. 4-to-3 TEG-DGA polyester; acid Number = 16; 6,000 cps (25°C)
4. 4-to-3 TEG-DGA polyester; acid Number = 12.5; 7,400 cps (25°C)
5. 6-to-5 polycarbonate of DEG and phosgene-59,000 cps (25°C).

It should be noted that polymer 5 had an unusually high viscosity based on prior preparations of this polymer.

A yellow flame composition (15 Mg, 65 NaNO_3 , 20 binder) was formulated with each polymer. At room temperatures, only hand mixes containing polymers 3 or 4, the lowest viscosity resins, gave castable systems. When the tests were repeated at 140°F (a standard mixing temperature for solid propellants), all systems were castable with those containing 1, 2, and 3 being preferred. The two lowest viscosity combinations exhibited evidence of some solid separation under these processing conditions.

SECTION IV

CONCLUSIONS AND RECOMMENDATIONS

This program has demonstrated that liquid, high oxygen-content polymers can be prepared and that they can be cured with suitable curatives under relatively mild conditions to give products with excellent mechanical properties. These polymers and curatives are compatible with pyrotechnic ingredients, and preliminary studies indicate that castable systems can be obtained with such binders.

While the program represents a most successful step toward a castable system, more remains to be done before either or both of these systems can be employed for obtaining castable pyrotechnics. At this point, the polymerization process, particularly that of the polycarbonate, has been examined only to the extent that a liquid product can be produced in reasonable yield. The only glycol studied to even this degree is diethylene glycol. Control of molecular weight, which is obviously a dominant factor in the viscosity of the polymer, has been examined only in a preliminary manner at best. It will be necessary to initiate a study of the preparation of the polycarbonate in which the effect of the glycol type, other reactants, changes in stoichiometry, reaction conditions, and workup procedure on the properties and the amount of the product obtained will be determined. With this accomplished, the behavior of pyrotechnic composition containing such binders must be evaluated in regard to the ballistic characteristics and mechanical properties immediately after manufacture.

The effect of aging with and without heating and agitation must also be evaluated in regard to both ballistics and mechanical properties. Any shortcomings of the binders that this study uncovers will require an effort of chemical modification of the polymers to correct this situation. Whether the polymerization process or the evaluation of pyrotechnics containing polymers prepared by the current method should be studied first is a matter of less importance than the recognition that both efforts are needed.

When the two programs discussed above have been completed, the castability of pyrotechnic compositions will have been demonstrated, the suitability of the pyrotechnic and mechanical properties established, and the polymerization process refined to produce significant quantities of the polymers. At that point, the stage will have been set for initiation of those studies by which a promising approach, such as these binders, can be converted to a practical end item for inclusion in the military arsenal of pyrotechnic devices.

SECTION V

EXPERIMENTAL

MATERIALS

1. Diglycolic acid - Practical grade - Columbia Chemical
2. Diethylene glycol - Chemical grade - Eastman
3. Ethylene glycol - Chemical grade - Eastman
4. Triethylene glycol - Chemical grade - Eastman
5. Butyl acrylate - Chemical grade - Eastman
6. Methyl acrylate - Chemical grade - Eastman
7. Vinyl acetate - Chemical grade - Eastman

All chemicals were used as received.

PREPARATION OF POLYESTERS

DEG (95.5 g; 0.9 mole) and 100 g (0.75 mole) of diglycolic acid were placed in a 500-ml three-necked flask equipped with stirrer and thermometer. The reaction was heated to 180°C and maintained at this temperature. Samples were removed hourly until the acid number of the product reached 20. Acid number was determined by dissolving a weighed sample of the polymer in equal volumes of benzene and methanol. A titration indicator, bromthymol blue, was added (10 drops). The solution was titrated with a standard 0.5 N potassium hydroxide. To calculate acid number, the following equation was used:

$$\text{Acid Number} = \frac{(\text{mls of KOH})(\text{mg of KOH per ml}^*)}{\text{Wt of sample}}$$

*For 0.5 N KOH, this equals 28.

When the acid number had reached the desired value, the reaction was terminated. To ensure that no water remained in the polymer, the product (a light yellow to brown colored liquid) was placed on a Rinco evaporator and stripped at full vacuum at 70°C for 4 hours. Table V lists typical polyester preparations.

PREPARATION OF POLYCARBONATES

Diethylene glycol, 764.4 g (7.2 moles), 1200-ml pyridine, and 2040-ml benzene were placed in a 5-liter three-necked flask, equipped with a stirrer, thermometer, gas inlet, and outlet attachments. A gas-metering apparatus was connected upstream from the gas inlet. Downstream of the gas outlet was a bubble device. The apparatus was swept with nitrogen for approximately 10 minutes to remove any moisture. The reaction mixture was cooled to 10°C, and 594 g (6.0 moles) of phosgene was bubbled into the flask (above the liquid) at such a rate that the reaction temperature remained below 15°C. The reaction became cloudy as the pyridine hydrochloride was formed and ultimately precipitated from solution. After addition of phosgene was complete, the reaction mixture was allowed to warm to ambient temperature and then was heated at 80°C

TABLE V. PREPARATION OF POLYESTERS

Book No.	Reactants	Molar Ratio	Acid Number	Viscosity, cps	Remarks
9668-6	Diglycolic - DEG	5:6	31	21,000	Molecular weight = 777
9668-7	Diglycolic - DEG	5:6	48	5,500	Molecular weight = 600 Analysis: C = 45.78, H = 6.33
9668-30	Diglycolic - DEG	5:6	20	--	5x scaleup of -6
9668-32	Diglycolic - DEG	5:6	48	--	5x scaleup of -7
9754-17	Diglycolic - TEG	5:6	7	16,500	
9754-17	Diglycolic - TEG	3:4	8	15,800	
9754-18	Diglycolic - TEG	5:6	22	10,000	
9754-20	Diglycolic - TEG	3:4	13	7,900	
9754-20	Diglycolic - TEG	3:4	16	6,000	

for 1 hour. Finally, the reaction was stirred overnight at ambient temperature under a slow nitrogen purge.

The reaction mixture was filtered under a nitrogen blanket to remove pyridinium hydrochloride. The filter cake was triturated several times with methylene chloride and refiltered. If the filtrate became cloudy, it was filtered. The filtrate was stripped first with a nitrogen sweep, and finally in the Rinco evaporator at full vacuum at 55 C for 3 hours.

The resulting liquid was dissolved in methylene chloride and washed several times with equal volumes of a 1-percent sodium hydroxide solution until the pH of the bottom layer containing the polymer was 8. This layer was then washed with water to remove traces of the base. The resulting liquid was then reduced in volume under a nitrogen sweep and finally stripped at 80 C under full vacuum on a Rinco evaporator for 4 hours to yield liquids with a yellow cast. Table VI lists typical polycarbonate preparations.

PREPARATION OF HIGH OXYGEN CONTENT ACRYLATE COPOLYMER

Preparation of Terpolymer

Butyl acrylate, 96 g (0.75 mole), 21.5 g (0.25 mole) of methyl acrylate, and 86 g (1.0 mole) of vinyl acetate were placed in a three-necked flask containing 300 ml of water, 4 g Dupont ME, 2 g of ammonium persulfate, and 10 g of dodecyl mercaptan. Attached to the flask was a stirrer, reflux condenser, and thermometer. The reaction mixture was heated with stirring to 70 C at which refluxing commenced. The heating mantle was removed, and the temperature continued to rise as the polymerization continued. If refluxing and temperature increase became too rapid, the mixture was cooled to 75 C. After refluxing had ceased (approximately 1-1/2 hours), the reaction mixture was heated for an additional hour at 90°C. The reaction was cooled to 60 C and then poured into a saturated solution of sodium chloride. A taffy-like solid separated. This solid was dissolved in benzene. The water layer, if present, was removed. The benzene solution was stripped at 70°C under full vacuum on a Rinco evaporator. A tan-colored liquid was obtained. The infrared spectrum is shown in Figure 3.

Hydrolysis of Acetate Groups on the Terpolymer

Butanol (150 g) (2 moles) was placed in a three-necked flask equipped with stirrer and thermometer. Under nitrogen, 1.8 g (0.075 mole) of sodium metal was added with stirring. A slight temperature rise was observed.

To a flask containing a mixture of 80 g of the terpolymer (described above) in 450 g of dry benzene was added to the butanol solution of sodium butoxide. An amber color developed immediately, and the solution became viscous. The reaction mixture was stirred overnight at ambient. Eight g acetic acid were added to the solution (the color became lighter), and the mixture was stirred for an additional 2 hours. The reaction mixture was poured into a large excess of water. Emulsion problems that were encountered were overcome by the addition of sodium chloride. The polymer layer was washed three times with water and then stripped on a Rinco evaporator. The product was a yellow taffy. (See Figure 4 for infrared spectrum.)

TABLE VI. PREPARATION OF POLYCARBONATES

Bock No.	Reactants	Molar Ratio	Viscosity, cps	Remarks
9668-4	DEG - Phosgene	6:5	6,800	85-percent yield
9668-11	DEG - Phosgene	6:5	12,500	76.9-percent yield, molecular weight = 721 Analysis C44.93 percent, H-6.34 percent
9668-14	DEG - Phosgene	6:5	14,000	Prepared in chloroform, 50.5-percent yield
9668-16	DEG-EG - Phosgene	3:3-5	1,235	52.5-percent yield, analysis C-43.46 percent, H-6.06-percent
9668-17	DEG - Phosgene	6-5	32,000	57-percent yield
9668-26	EG - Phosgene	6-5		40.5 percent yield, molecular weight = 120 Analysis-C-40.7 percent, H-4.55 percent
9668-28	Repeat of -16		7,600	
9668-36	DEG - Phosgene	11-10	50,000	68-percent yield
9668-49	DEG - Ethylene Bischloroformate		480,000	Molecular weight = 665, analysis = C-43.87 percent, H=5.86 percent
9668-49	EG - Ethylene Bischloroformate		935,000	
9754-16	TEG - Phosgene	6:5	26,500	
9754-18	DEG - Phosgene	4:3	30,200	
9754-21	TEG - Phosgene	4:3	12,000	

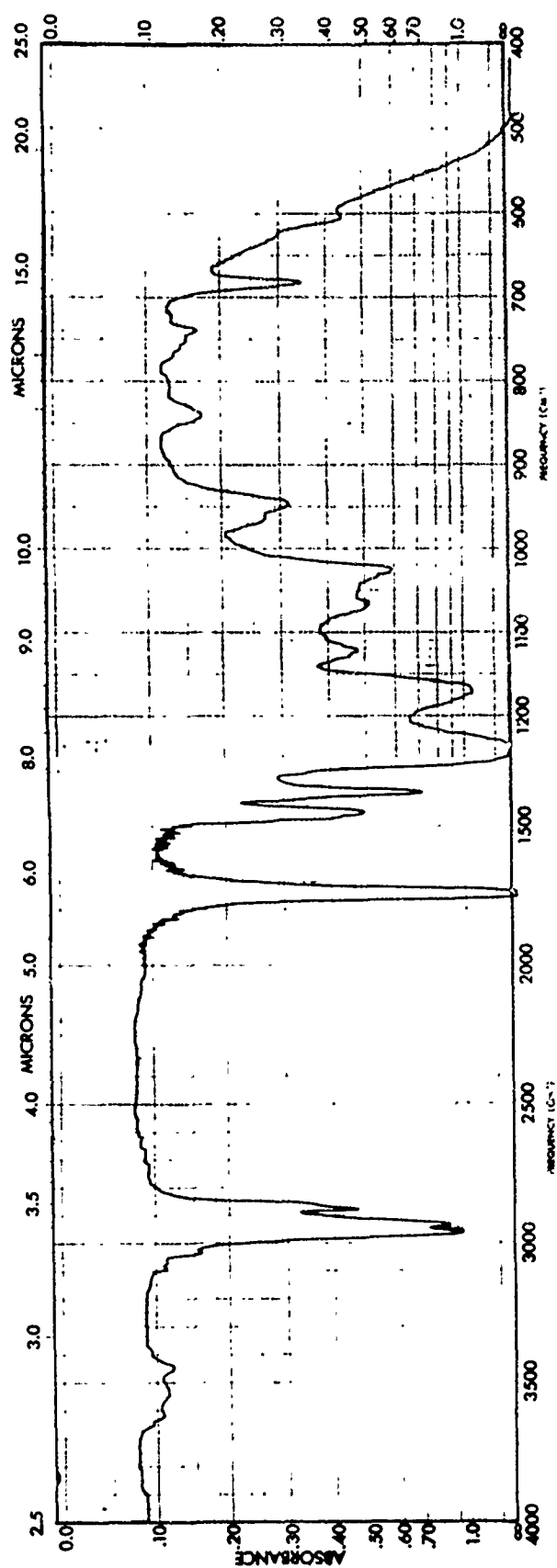


Figure 3 Terpolymer of Butyl Acrylate, Methyl Acrylate, and Vinyl Acetate

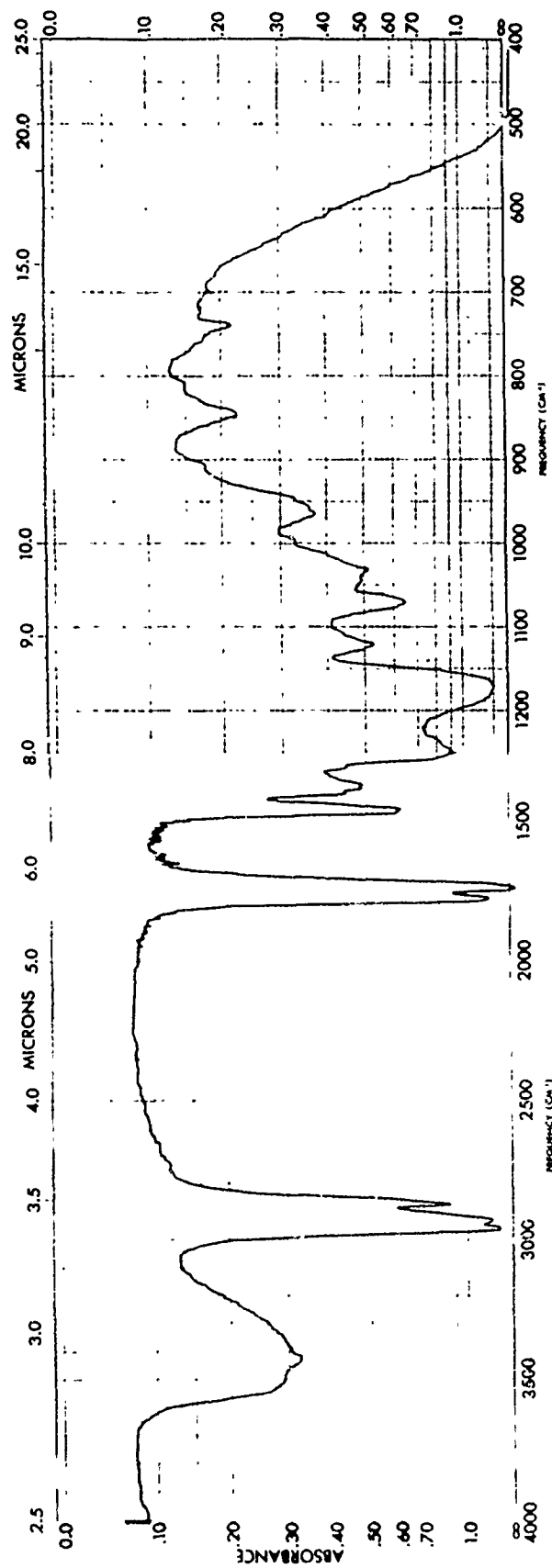


Figure 4. Product From the Hydrolysis of Acetate Groups on the Terpolymer

Esterification of Hydrolyzed Product

The hydrolyzed product from 2 (20 g) dissolved in 110 g of acetic anhydride was cooled to 0°C. Eight moles of white fuming nitric acid were added dropwise over a period of 30 minutes. The resulting clear solution was then stirred an additional 1-1/2 hours at 0°C. The reaction mixture was poured onto 800 ml of ice which yielded a yellow oil. The oil was extracted with methylene chloride. The combined extracts were thoroughly washed with 5-percent sodium hydroxide and finally with water. After drying with MgSO_4 , the solvent was removed by means of a Rinco rotary evaporator yielding 15 g of a yellow taffy. Its infrared spectrum (Figure 5) was consistent with the proposed structure in that hydroxyl peak obtained for the hydrolyzed copolymer had disappeared and a strong nitrate ester peak was present.

Typical runs for the acrylate copolymer approaches are given in Table VII.

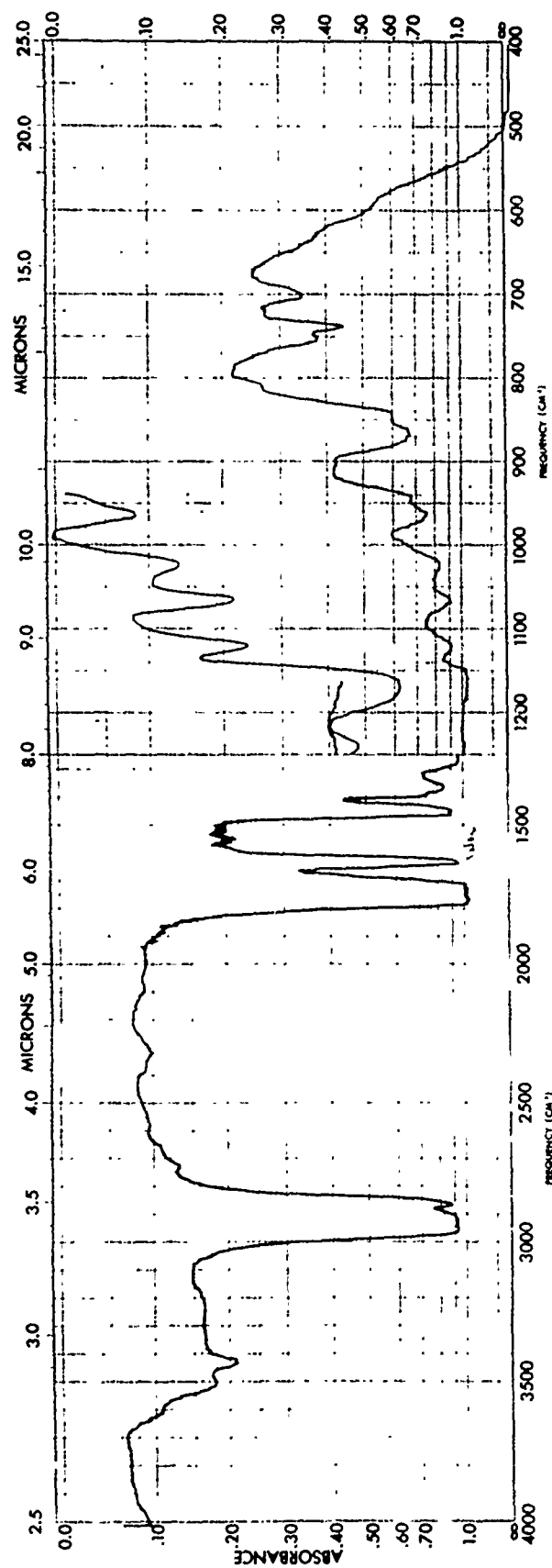


Figure 5. Product of Esterification of the Hydrolyzed Terpolymer

TABLE VII. PREPARATION OF ACRYLATE COPOLYMERS

Book No.	Reactants	Molar Ratio	Remarks
9668-1	Ethyl Acrylate-Vinyl Acetate	1 to 1	75-percent conversion, solid
9668-2	Ethyl Acrylate-Vinyl Acetate	1 to 1	Doubled chain transfer agent content, no effect on viscosity, solid
9668-12	Ethyl Acrylate: Vinyl Acetate	1 to 1	Emulsion polymerization, 100 percent conversion, solid
9668-21	Butyl Acrylate: Methyl Acrylate: Vinyl Acetate	0.75 to 0.25 to 1	100-percent yield, taffy
9668-22	Butyl Acrylate: Methyl Acrylate: Vinyl Acetate	0.75 to 0.25 to 1	Doubled chain transfer agent content, liquid, 199,000 cps
9668-31	Hydrolysis - 21		Taffy
9668-40	Esterification of 31		Taffy

APPENDIX I

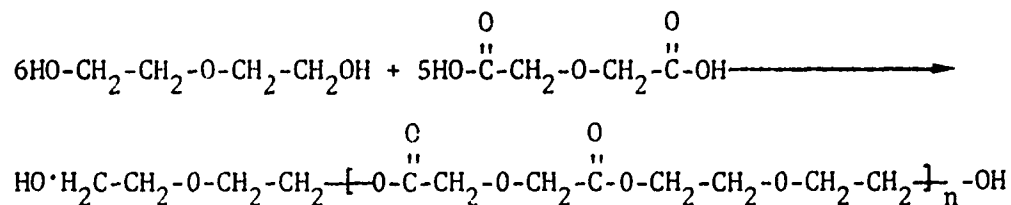
CHARACTERIZATION REPORT

I. POLYMER PROPERTIES

A. Polyester - PE-101

1. Preparation - reaction of diethylene glycol and diglycolic acid.

Stoichiometry - 6 glycol to 5 diacid.



2. Acid Number - 17 (determined by titration)

3. Elemental Analysis -	<u>Determined</u>	<u>Calculated</u>
Carbon	45.78	46.9
Hydrogen	6.33	6.2
Oxygen (by difference)	47.89	46.9

4. Molecular Weight (by ebulliometry) 877 (calculated - 1126)

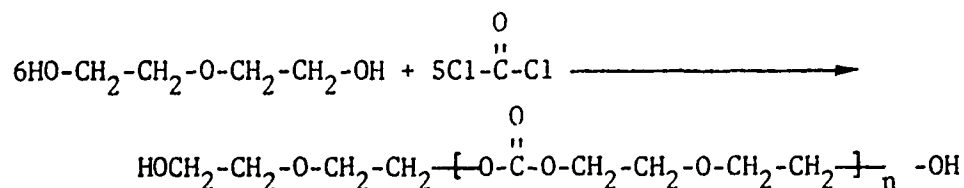
5. Infrared Spectrum - Figure 1

6. Viscosity (Brookfield, 23°C) - 35,200 cps

B. Polycarbonate - PC-101

1. Preparation - reaction of diethylene glycol and phosgene.

Stoichiometry - 6 glycol to 5 phosgene



2. Elemental Analysis -	<u>Determined</u>	<u>Calculated</u>
Carbon	44.90	45.4
Hydrogen	6.52	6.5
Oxygen (by difference)	48.58	48.1
3. Molecular Weight (by ebulliometry)		
729 (calculated - 766)		
4. Infrared Spectrum - Figure 2		
5. Viscosity (Brookfield, 23°C) - 23,000 cps		

II. CURING PARAMETERS

- A. Procedure - polymer and curative mixed at various OH/NCO equivalent ratios, time and temperature of cure cycle varied, cure determined by degree of consolidation of sample.
- B. Curing Reaction - For both polymers, reaction of hydroxyl groups of polymer with a polyisocyanate.



- C. Curative employed for both polymers - PAPI
- D. Recommended Curing Schedule (for both polymers)

1. Stoichiometry - 1-to-1 hydroxyl/isocyanate

Oxygen Content of Polymer - Curative Combination -

Polyester PE-101 - 1.0 g polymer - 0.25 g PAPI; $[\text{O}] = 40.5$ percent
(Calculated)

Polycarbonate PC-101 - 1.0 g polymer - 0.36 g PAPI;
 $[\text{O}]$ (Calculated) = 39.0 percent

2. Cure Temperature - Ambient
3. Cure Time - 72 hours

E. Pot Life of Polymer - Curative mixture (25°C)

Brookfield Viscosity, cps after

Polymer	0 Hour	1 Hour	2 Hours	4 Hours	5 Hours	6 Hours
Polyester	15,400	950,000	1,800,000	2,900,000	4,000,000	4,400,000
Polycarbonate	8,200	330,000	1,600,000	3,920,000	6,720,000	7,440,000

F. Peak Exotherm - 100-g polymer mixed with requisite amount of curative - for polyester - 25 g PAPI; for polycarbonate - 36 g PAPI

- initial temperature - 79°F (for both polymers)

- peak temperature (during 24-hour period) - 80°F (for both polymers)

III. MECHANICAL PROPERTIES OF CURED SYSTEMS

A. Procedure - polymer and curative mixed at 1-to-1 OH/NCO ratio, cast into appropriate specimen containers (see below), cured as per schedule listed above, then tested.

B. Specimens Employed

1. Tensile - Elongation - Dogbone - gage length - 1.70 inches, cross section 1/4 by 1/4 inch

2. Compression - 1 inch cube

3. Shrinkage - 1/2 by 1/2 by 5 inches

Mechanical Property

Polymer	Tension Strength, psi	Elongation, %	Compressive Strength, psi	Strength, % Change
Polyester	50 ^a	1100 ^a	> 7500	< 1 ^b
Polycarbonate	62	480	> 7500	< 1 ^b

^aSlightly undercured sample

^bEstimated value due to rubbery nature of product

IV. COMPATIBILITY TESTS

A. Spot Plate Tests - individual ingredient mixed with polymer in spot plate at ambient temperature, observed one hour for bubbling or discoloration

1. Ingredients Employed

Potassium chlorate

Strontium chloride

Barium chloride

Potassium perchlorate

Sodium nitrate

Barium nitrate

Magnesium (4 grades)

2. Results - No reaction observed for either polymer with any ingredient. PAPI evaluated with all ingredients - no reaction.

- B. Hot Stage Microscope Tests - Ingredient mixed with polymer sample, transferred to microscope slide, and placed in hot stage of Richert Microscope, cavity closed and temperature raised to 250°F, visual observation throughout heating cycle.
1. Ingredients employed - same as in spot plate tests
 2. Results - no evidence of reaction
- C. Vacuum Stability Tests - Sample mixed, then transferred to ampoule, which is attached to a mercury gas buret, ampoule heated in oil bath at 70°C for 48 hours, gas evolution monitored. [Reference Table IV.]

NOTE: In solid propellant applications, gas evolution of less than 2 cc/g/48 hours is considered acceptable for compatibility.

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13. ABSTRACT <p>Low-cost liquid polymers of high oxygen content (>45 percent) have been prepared. Curing behavior of combinations of the polymers and cross-linking agents has been evaluated as well as the mechanical properties of the cured materials. Compatibility with pyrotechnic ingredients was determined as well as castability of pyrotechnic compositions containing such polymers. The high level of behavior exhibited by the polymer systems indicates that they possess considerable potential for use in the development of castable pyrotechnic formulations that will exhibit a high level of performance in regard to color quality and illumination.</p>			

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